https://dx.doi.org/10.22161/ijaers.4.2.25 *ISSN: 2349-6495(P) | 2456-1908(O)*

Enhancement Adsorption of Heavy Metal from Recovered Base Oil using Zeolite and kaolinite by Phase Transfer Catalyst and anionic surfactants-Part 2

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Abstract— *Recovery of used lubricating oil by extraction produced organic sludge and recovered base oil. This oil has metallic content such as magnesium, nickel, vanadium, iron, and zinc. In this study, the recovered base oil was treatment by using adsorption process to remove heavy metals Zeolite and kaolinite were used as an adsorbent with and without additives. The parameters investigated include contact time, amount of zeolite, and amount of the additive. The results showed that there is a synergism between zeolite and anionic additive, further more ash removal was higher than that in the prescience of the cationic additive. The optimum removal obtained were 98% and 92 % with anionic and the cationic additive respectively, while in case of kaolinite 87% and 82% respectively. is The most influential parameter affecting ash removal was the concentration of additives and time of adsorption. The results were discussed according to adsorption isotherm of heavy metals on phase transfer catalyst or the anionic additive in pore diameter of zeolite. The results showed that, viscosity increased from 30 cst for used lube oil to 68 cst while the density decreased from 912 to 900 kg/m3 and the pour point from -2 to −8.5 °C. The purification oil can be used again after distilled to light naphtha and middle distillate.*
Keywords— waste lubricating oil, adsorption, zeolite, phase transfer catalyst, synthetic fuel.

I. INTRODUCTION

The problem of protecting the environment from pollution and contamination by several of discharges is now in the focus of attention all over the world. Consequently, the reuse and recycle of used lubricating oil became the most ideal solution. Lubricating oils contains different pollutant such as additives, heavy metals. Among the treatment methods proposed like solvent extraction (1,2). The composition of typical waste lubricating oil is a stable dispersion of undergirded base oil and additives with high concentration of metals, varnish, gums and other asphaltic compounds from the overlay of bearing surfaces and cracking of the lubricating component. Solvent can be used as single or mixture in extraction processes. The efficiency of solvent extraction enhance by mixing more than one solvent. The base oil recovered by solvent contains metals (3). Adsorption method appears to offer the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds. In addition, because adsorption is generally reversible, the generation of the adsorbent with resultant economy of operation may be possible. The step prepares the used oil for extraction heavy metals. Large solids are removed by screening, a large number of types of filters have been developed (4). Then solvent extraction and heavy metals are removed by adsorption on kaolinite with and without anionic surfactant. Adsorption is a physico-chemical treatment process for extracted oil. This processes exploiting the ability of certain heavy metals and additives to adsorb on kaolinite surface. The adsorption processes is a powerful method for the environmental engineer and has many application (4). The adsorption of single metal ion was found to be little affected by the type of anion associated with it but the effect on mixed metal ions adsorption processes was found to be more pronounced. Recycle of used oil has been carried out by several methods. Concentrated sulphuric acid has been used to remove asphaltenic material. The product is vacuum distilled (5). The recycled oil contains higher amount of metals. Surfactant-based separation processes are an increasingly important method of separations for waste treatment application (6).This is due to these separations need much energy than traditional methods, such as distillation followed by extraction (6). Heavy metals are of particular important due to their toxicity and persistence in the environment (7). They can cause problems for humans and animals. There are several physico-chemical methods, such as coagulation-flocculation and chemical precipitation (8, 9). Consequently, research efforts have been directed towards adsorption using clay s and zeolite as an alternative technique for the removal of heavy metals. Kinetic studies of adsorption can carried out using the finite bath technique, where a large volume of the adsorbate is admixed with required weight of adsorbent. The

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performance of zeolite in the removal of heavy metals has been discussed in research literature and conclusions in relation to their treatment performance (9). Metallic compounds should be removed from used lubrication oil to obtain base oil suitable for the formulation of new lubricants. Removal of heavy metal such as nickel, vanadium, titanium, iron, magnesium and zinc from recovered base oil was detail in this research. The objective of this study evaluates kaolinite and zeolite as adsorbent for treatment extracted base oil by solvent to remove heavy metals. Furthermore, the effect of the anionic surfactant sodium salt of dodecyl diphenyl ether sulphonat as anionic surfactants (ANS) and tetraethyl ammonium bromide (TEB) which prepared early (10) on recovery heavy metals are discussed. The author studies the affect of different mole fractions of the additives on degree recovery heavy metals, and suggests the field of action mechanism of the extraction according to micelles.

II. MATERIALS AND METHODS

Feed

Waste lubricating oil was treated by filtration. The used oil was distilled under vacuum to remove water and low-boiling contaminants, and treating the dried oil with a different solvent mixture of butanol, hexane, benzene, isopropanol and methylethyl ketone which causes the separation of a layer of sludge containing contaminants of additives. The solvents were of analytical grade and supplied by E. Merck.

Extraction Process

A mixture of solvent and used lubricating oil was shaken in a 250 ml separating funnel. Solvent to oil ratio was 4:1(v/v). The sludge was allowed to settle at a constant temperature of 30C. After constant time, solvent-oil solution was separated from sludge. The sludge was washed twice with the same solvent to extract any remaining oil. The solvent was recovered by vacuum distillation. The yield of oil was calculated on the basis of initial mass of used oil taken. After solvent recovery, the desludged oil is then subjected to treatment with kaolinite and zeolite with or without dodecyl diphenyl ether sulphonat as anionic surfactants (ANS) and tetraethyl ammonium bromide (TEB) as cationic catalysis which prepared early. This method was demetalization by using beaker, water bath and electric stirring, complete stirring for 2 hours, separation adsorbent and recovered base oil after adsorption used centrifuge. Types of kaolinite, or zeolite as adsorbent to oil ratio, types of solvent and type of surfactants (anionic or cationic surfactants) to oil ratio through adsorption processes were varied. The solvent-oil solution was distilled under vacuum and total ash content was determined. Adsorbed oil was analyzed to determine ash content. Also carbon residue, viscosities at 40 and 100ºC and pour point were determined.

Demetalization by adsorption

Adsorption technique was used to de-metallization at different variables such as, type and particle size of sorbent, activation temperature and time were studied to obtain good quality oil with maximum yield. Ash contents in used lubricating oil were determined according ASTM D D 482 and metal content were analyzed by atomic adsorption

Choice of Sorbent

Effect of two well known sorbents kaolinite and zeolite on extracted oil were studied. Complete specification of kaolinite are shown in table 1, while zeolite are prepared and complete specification are published by author early (11).

Hexane was used as solvent in presence the anionic surfactant ANS and cationic catalysis TEB. These experiments have carried out to study the effect of adsorbent amounts on the rate of ash content , the following dose of adsorbent were 2,5,8,10 gm/100ml of oil and n- hexane as solvent, at temperature 30 C, 500 r.p.m agitation rate. The above agitation were changed 300, 600, 900, 1100 and 1200r.p.m. The equilibrium isotherm was studied by using fixed amount of adsorbent and stirring for two hours at 30 C^0 and 1200 r.p.m agitation rate .

Table.1: Complete specification of adsorbent kaolinite

Item	Composition%
SiO_2	45
TiO_2	1.5
Al_2O3	38
Fe_2O_3	0.5
MnO_2	0.5
MgO	0.34
CaO	0.5
Na_2O	0.05
K_2O	0.4
P_2O_5	0.3
L.O.1	13

III. RESULTS AND DISCUSSION

Use of these solvents is based on their capacity to form hydrogen bond. On comparing properties of used and extracted oil (Table 2), it is clear that specific gravity, carbon residue and % yield decrease with increasing sludge removal by solvents. The same trend is present in viscosity values at 40 and 100oC improvers. MEK has the best performance to remove these additives while other solvent are moderate in their efficiency. The ash value

shows the presence of metallic impurities which is reduced by 20-30% in extracted oil.

Table.2: Properties of used and solvent extracted oil at 30°C at solvent to oil ratio 4:1 after 12 hours settling

Property	**Used oil**	**Extracted oil using solvent extraction**				
		iso propanol	**Butanol**	**n-hexane**	**Benzene**	**MEK**
Specific gravity at 35oC ASTM D 1298	0.877	0.877	0.877	0.876	0.877	0.877
Viscosity at 40oC (cst) ASTM D445	103.50	67.5	67.6	68.7	67.7	70.5
Viscosity at 100oC (cst) ASTM D445	14.50	8.53	8.56	9.25	9.42	10.21
Carbon residue (wt%) ASTM D 189	1.832	1.5	1.6	1.7	0.9	0.88
% ASH content ASTM D482-80	1.2	1.05	1.03	1.01	0.98	0.95
Yield %	-	95.5	95.5	96	94.2	92.9

A sample of kaolinite with size 100 mesh is analysed and the composition of this constituents are shown in Table 1 and used as adsorbent to decrease ash content% in extracted lube oil.

The results show reduction of ash percentage in all experiments. Fig.1 represents the ash content in used oil after adsorption with different dose of kaolinite and zeolite without additives and with 0.001% of additives (above cmc).The results confirm addition the anionic additive ANS enhance depletion of ash content rather than using cationic catalysis TEB. It should be noted that the amount of ANS or TEB required to demetallized waste oil depend on its ash content. The higher ash content means that reaction between additive and heavy metals are small. Increasing kaolinite concentration increases the amount of available sorption sites. Therefore, heavy metals sorption increase with increasing kaolinite and consequently decrease ash content. Increasing zeolite or kaolinite concentration increases the amount of available sorbtion sites. In addition, ash content% decrease at high zeolite or kaolinite concentration since it reduces the competation betwee metal ions due to the availability of more sorption sites on its surface. In addition, the anionic ANS enhance heavy metal adsorption rates at surface of kaolinite. But the degree of enhancing decreases with using the additive TEB. This result depends on the charge of heavy metal, which confirms the charge of heavy metals is positive. The force between the anionic additives is attractive while repulsion with the cationic additives. On the other hands, using zeolite instead kaolinite lead to increasing the amount of sorption through pore surface. In addition, heavy metal sorption rates increase at high sorbent concentration. However, addition 0.001% of additives ANS or TEB decrease the ash content in recovered lube oil, which successively affects the removal of heavy metals. The author suggested that this may be due to the increased diffusion of heavy metal ions into zeolite pores. Also it increased with the increase in the specific surface area of zeolite. At optimum conditions, 10gm of kaolinite or zeolite, temperature 30, stirring 1200r.p.m and 0.001of the additive the kinetic data is shown in Table 3.

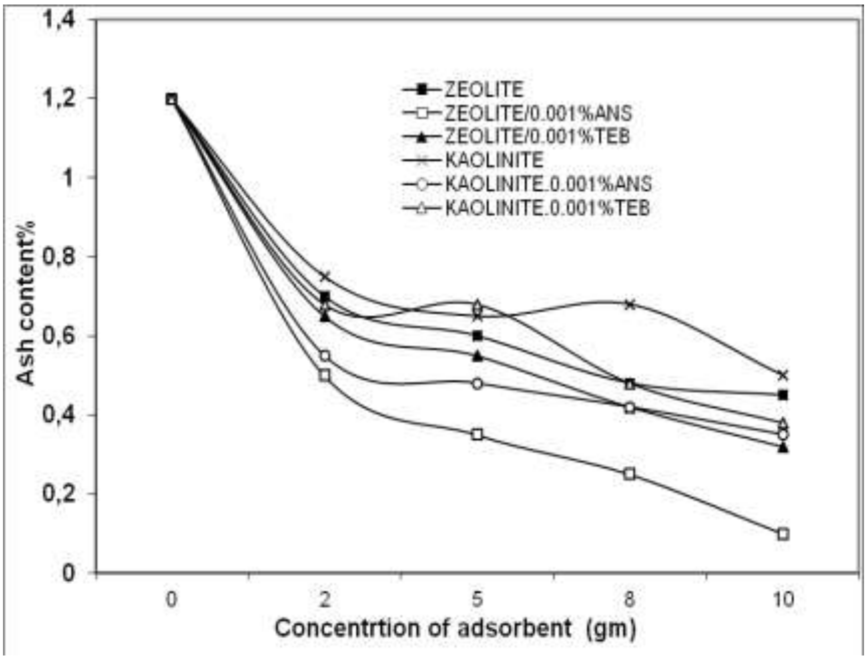

Fig.1: Effect of concentration of adsorbents with or without additives on ash content% on extracted used lube oil

https://dx.doi.org/10.22161/ijaers.4.2.25 ISSN: 2349-6495(P) | 2456-1908(O)

Table.3: Kinetic study the effect of time of adsorption on ash content in extracted lube oil using different adsorbents.

Time (min)	Pure adsorbent				Adsorbent with the additive			
	Kaolinite		Zeolite		Kaolinite		Zeolite	
	C g/L	C/C^0	C gm/L	C/C^0	0.001 ANS	0.001% TEB	0.001% ANS	0.001% TEB
20	0.85	0.708	0.75	0.625	0.50	0.58	0.40	0.55
30	0.80	0.666	0.70	0.583	0.40	0.46	0.30	0.43
50	0.78	0.65	0.69	0.575	0.30	0.39	0.20	0.32
60	0.76	0.633	0.65	0.541	0.28	0.37	0.18	0.30
90	0.65	0.541	0.55	0.458	0.15	0.36	0.09	0.28
100	0.57	0.475	0.51	0.425	0.09	0.25	0.06	0.25
120	0.51	0.425	0.45	0.375	0.06	0.20	0.04	0.19

The rate of ash removal increases with increasing time and depend on the type of additive. These results confirm zeolite prefer in removal heavy metal in the presence of ANS. This result can be discussed according the surface area and pore size in surface of zeolite, so adsorption take place through pore rather than surface adsorption. The active sites, can be present inside the pores of zeolite. . However, action can be enhance enter into the porous structure by additive, which prefer the anomic ANS rather the cationic TEB. The pore size of this zeolite about 0.45 nm. These results compatible with Wang et al (12). He reported that the removal of heavy metals increased with the increase in the specific surface of zeolite. Similar observations have been reported by other researchers (13). The equilibrium results of decreasing ash by zeolite or kaolinite with or without additive are shown in Table 3.

The percentage of decreasing ash content in used oil differ with varying the type and dose of the additive at optimum conditions as shown in table 4
.

Table.4: Effect of varying dose of the additive on efficiency of reducing percentage of ash% .and degree of surface coverage.

Additive Percentage %	**Kaolinite**				**Zeolite**			
	ANS		**TEB**		**ANS**		**TEB**	
	% Removal ash	**θ**	**%Removal ash**	**θ**	**%Removal ash**	**θ**	**%Removal ash**	**θ**
0.0001	65	0.65	60	0.60	72	0.72	70	0.70
0.001	70	0.70	68	0.68	82	0.82	78	0.78
0.005	82	0.82	75	0.75	92	0.92	87	0.87
0.01	85	0.85	79	0.79	95	0.95	90	0.90
0.05	87	0.87	82	0.82	98	0.98	92	0.92
0.1	85	0.85	81	0.85	92	0.92	91	0.91

The results show the rise of the decreasing ash% represents the formation of the first layer of the adsorbate on the adsorbent surface. Then, all possible sites in the surface are filled and further adsorption stop, these clear from degree of surface coverage by additives. A micelle composed of the anionic ANS or the cationic TEB in oil medium, the concentration of counterions (heavy metals cations) opposite to that of the surfactant. As the results, adsorption be considered at the adsorption at the micelle-oil interface. These adsorbed counterions are either bound in the stern layer of the micelle. The complete chemical analysis of the treatment oil are listed in the following table (5).

Table.5: Complete chemical analysis of the treatment oil by zeolite or kaolinite.

Property	Used oil
Specific gravity at 35oC ASTM D 1298	900 kg/m3
Viscosity at 40oC (cst) ASTM D445	130.50
Viscosity at 100oC (cst) ASTM D445	68 cst
Carbon residue (wt%) ASTM D 189	0.8
% ASH content ASTM D482-80	0.06
Pour point ASTM D 97	−8.5 °C

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The results show lube oil become available to re -use after enhance its specification and decreasing ash content of heavy metals%. Further work needs to study complete chemical analysis of heavy metal in the next research.

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